

Electrodeposited Tungsten-Nickel-Boron-A Replacement for Hexavalent Chromium

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Chromium, deposited from acidic solutions of its hexavalent ion, has been the rule for wear resistant, corrosion resistant coatings for many years. Although chromium coatings are durable, the plating process generates air emissions, effluent rinse waters, and process solutions that are toxic, suspected carcinogens, and a risk to human health and the environment. Tungsten–nickel–boron (W–Ni–B) alloy deposition is a potential substitute for hexavalent chrome. It has excellent wear, corrosion, and mechanical properties and also may be less of an environmental risk. Our study examines the electroplating process and deposit properties of W–Ni–B and compares them with those of hexavalent chrome.

Deposit Description

The W–Ni–B alloy composition is 39.5% tungsten, 59.5% nickel, and 1% boron. Thicknesses between 1.0 and 250 microns can readily be deposited. The deposit's nanocrystalline structure has a grain size so small that it has been defined as glass-like or amorphous. The deposit is highly reflective, replicates the substrate, and has the color and appearance of polished silver or rhodium.

Process Description

The plating solution is a mixture of sodium tungstate, nickel sulfate, and sodium borate. The pH is adjusted with ammonium hydroxide to 8.4. The ammonia also helps to chelate the metal ions and stabilize the bath. The process uses insoluble, 300-series stainless-steel anodes. The anodes can either be placed in membrane baskets to prevent electrolyte oxidation or used directly in the solution. Using them directly, without the membrane barrier, requires periodic carbon treatment to remove the brightener breakdown by-products.

The process operates at 120° F, regulated either with steam coils or electric immersion heaters. Agitation and filtration of the solution is essential to insure alloy uniformity and also to reduce roughness in the deposit caused by suspended particulate matter.

Cathode current density is varied from 36 to 100 amp/ft² (amps per square foot of work area) according to the shape of the article being plated and the rate of deposition required. The alloy composition and structure are not appreciably affected by changes in current density.

Process Operation

The solution is prepared in a working tank from concentrate AMPLATE UA-B, manufactured by Fidelity Chemical Company, and the operating level is adjusted using deionized water. The tank, pump, piping, filter cartridge, anodes, and associated equipment are all precleaned and leached with a 2% solution of ammonium hydroxide and water. After filling the tank, the filter pumps are turned on and adjusted to provide a minimum of two solution turnovers per hour and to maximize the electrolyte movement at the cathode.

Plating can proceed, after heating the solution to 120° F and adding the proper brightening and wetting agents. The cathode efficiency is about 38% depending on the current density and electrolyte replenishment through the double layer at the cathode. We obtained plating rates above 0.002 inches per hour by increasing the current density (see Figure 1).

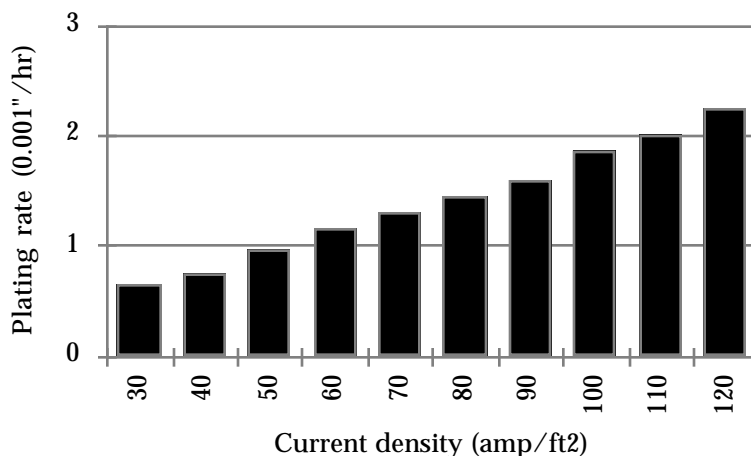


Figure 1. Plating rate.

We used sodium laurel sulfate to reduce the surface tension at the cathode and allow the hydrogen bubbles that are produced in the process to be easily released. No air agitation was used because it would make the wetting agent foam and speed up oxidation of the sodium tungstate. Leaks in the filter pump system were eliminated whenever possible because air injection from such leaks would also cause foaming and tungstate conversion.

Chemicals need to be replenished during the plating process because insoluble anodes are used. Soluble anodes, if they were available, would replenish the metal salts and avoid oxidizing the brightener and wetting agent chemistries. Chemical replenishment can be done automatically using amp-hour metering pumps or manually after chemical analysis. The amp-hour metering pumps add chemicals as the work is processed through the solution, which reduces the need for analytical support.

Deposit properties

We tested one plating solution with brightened chemistry (UA-B). The brightened bath creates thinner deposits to give maximum reflectivity. An unbrightened solution is used for thicker industrial deposits; however, we did not test an unbrightened solution.

Throwing power. We determined throwing power using 2- by 16-inch copper panels with a 90 degree bend 8 inches from one end. Throwing power was measured by the ability of the bath to completely plate the inside corner of the bend. We then compared the throwing power of this bath with that of a hexavalent chromium bath. The results are shown in Figure 2.

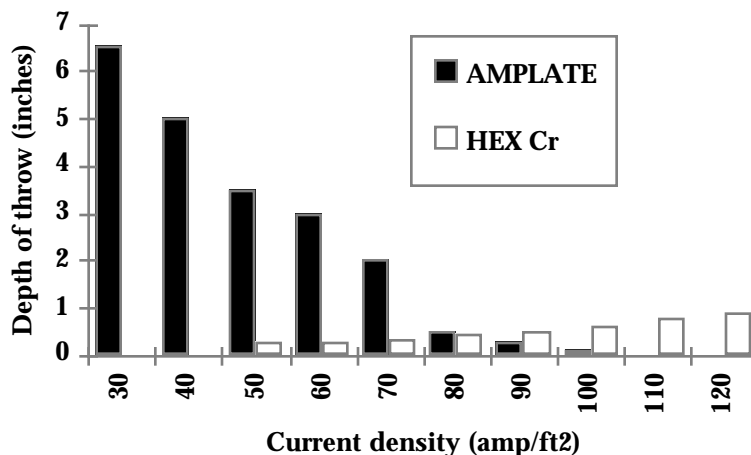


Figure 2. Throwing Power

Color Uniformity. We determined color uniformity by plating a polished copper panel and comparing color versus thickness. Table 1 depicts the results and compares them with those of a hexavalent chromium deposit.

Table 1. Color uniformity

Amp/ft²	W-Ni-B (AMPLATE)	Hexavalent Chromium
30	bright	no plate
40	bright	no plate
50	bright	no plate
60	bright	no plate
70	bright	dull
80	bright	dull
90	bright	frost
100	bright/frost	frost
110	frost	bright
120	frost/burnt	bright

Reflectivity. Reflectivity was determined for varying deposit thicknesses on a polished copper panel. Light impinged on the surface at an angle of incidence of 5 degrees from perpendicular, and the detector measured the intensity of light with an angle of reflection of 5 degrees. We used a mixture of wavelengths that corresponded to natural sunlight. The values were compared to those of a hexavalent chromium deposit and appear in Table 2.

Table 2. Reflectivity

Amp/ft²	W-Ni-B (AMPLATE)	Hexavalent Chromium
30	0.64	no plate
40	0.65	no plate
50	0.65	no plate
60	0.65	no plate
70	0.66	0.3
80	0.66	0.3
90	0.65	0.35
100	0.65	0.38
110	0.6	0.48
120	0.55	0.51

Corrosion Resistance. Using acids of varying concentrations, we made corrosion resistance tests on W-Ni-B deposits, hexavalent chromium, and phosphorous electroless nickel. Table 3 shows corrosion times extrapolated to 0.001 inches per year weight loss.

Table 3. Corrosion times.

Acid	W-Ni-B (AMPLATE)	Hexavalent chromium	11% Phosphorous electroless nickel
25% HCL	0.25	100	1
25% H2SO4	0.25	25	0.75
25% HNO3	0.65	0.1	80
48% HBF4	0.1	0.2	1.5
5% H3PO4	0.3	4	0.8

Stripping and Repair. The deposit was stripped in a proprietary 10 grams per liter oxidizing, chelated alkali solution designed for electroless nickel. This process produces some smut that must be brushed from the part to prevent inhibition of the stripping action. The stripping rate was 0.001 inch per hour at 160° F.

Machinability. We are still studying whether or not the W-Ni-B deposit can be diamond-turned with low tool wear. Initial tests indicate that it may be possible to produce high-quality surfaces for optical mirrors with this technique.

Conclusion

Amorphous deposits of W-Ni-B can be deposited from an alkaline bath using insoluble anodes. The deposits compare favorably with hexavalent chrome deposits in throwing power, color uniformity, reflectivity, and corrosion resistance. We are still studying machinability. The useful life of the solution has not been determined, but carbon treatment should allow the bath to operate efficiently for many thousand amp hours. The deposits are sound and appear to offer an excellent alternative to chromium deposited from hexavalent chemistry.

A useful follow-on study would be to evaluate how the use of W-Ni-B chemistries affects worker health and the environment when compared to hexavalent chromium.

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